A STUDY OF OXYGEN DIFFUSION THROUGH FROZEN FOOD PACKAGING MATERIALS

by

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B. S., Kansas State College
of Agriculture and Applied Science, 1949

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Horticulture

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1951

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INTRODUCTION

In any consideration of the characteristics desired in a frozen food container, the two factors moisture-vapor-proof and resistance to penetration of gases, especially oxygen, are almost always listed. The prevention of oxidative changes during freezing and storage is one of the outstanding problems of the frozen food industry.

There is no lack of variety among the frozen food containers available on the market. They vary from glass jars, through rigid paperboard cartons and enamel lined tin cans, to flexible pouches. Knowing that the average housewife is led to the use of paperboard and film-liner containers by the considerations of cost and convenience, it was thought desirable to determine the relative value of these containers as a barrier to oxygen penetration.

Two types of rigid paperboard cartons and three types of flexible, film liner bags were selected for testing. A common ice cream carton and a glass beaker were also included as controls. At the beginning of the experiment, it was hoped that a scale of values could be found ranging from the most impermeable to the very permeable containers.

After a few preliminary runs had been made, it became evident that there was a distinct difference between values obtained by testing the seal made in the home or laboratory as compared to the factory sealed ends of some containers. The design of

the experiment was therefore varied to test the seal made in the laboratory. In the case of the film bags, all three types were heat-sealed by the use of a hot flatiron. The rigid cartons were first tested by just fitting the lids on, then another series was run using a special wax preparation, in an attempt to completely seal the lids. It seemed obvious that the best material was no more efficient than its poorest seal, and although this course of experimentation was a modification of the original intent, it was hoped that it would prove to be a valuable study.

To all intents and purposes, this was not a conclusive study of oxygen permeability in frozen food containers. Many types of containers were not tested, and those that were, need to have further tests of a more tangible nature. It is hoped that some addition has been made to available knowledge, and furthermore, that it will serve as a stimulus to more extensive experimentation.

REVIEW OF LITERATURE

Most of the early work done on the mechanism of diffusion came about through investigations of balloon fabrics. These fabrics were a combination of some type material with rubber coatings between layers of the material and on the outside. Gas could escape from these envelopes through leaks in valves, seams, and imperfections in the fabric, as well as through the fabric itself.

The next step in the study of diffusion resulted from in-

terest in pneumatic tires for automobiles and has developed from there to the various ramifications of materials and usages found today.

Edwards (1918) suggested that hydrogen might pass through a balloon fabric by diffusion through minute holes, similar to the passage of gas through a porous plate, or by solution in the rubber film with subsequent evaporation from the other side. He reported work done by Graham in 1866 which showed the flow of gases through rubber films to be a solution phenomenon and not a diffusion phenomenon. Edwards continued, "It has been known for a long time that the permeability of rubber films increases rapidly with increase in temperature" and that "the change in permeability with change in pressure is very small." He also thought the amount of water dissolved in the rubber probably influences the rate of penetration of rubber by hydrogen.

Two years later, Daynes (1920) listed two suggestions as to how a rubber film formed an obstacle to the passage of gas. One was to the effect that the material itself forms a barrier and the gas can pass the surfaces of the film quite readily. The other stated the chief obstacle as being the surface, the thickness of film having very little effect. He made a distinction between a gas passing through a membrane into a vacuum and a gas permeating into another gas. According to Daynes, "It has been shown that absorption is proportional to the gas pressure." He made the following general assumptions concerning the rubber membrane he tested.

1. That absorption of a gas is proportional to partial pressure, independent of pressure of any other gas.

2. That there is no appreciable resistance at the surface to the passage of any gas.

3. Different gases present do not appreciably impede one another in passing through the rubber.

Rowley (1939) believed there were at least three types of materials in relation to the passage of vapor through solid materials. Those which are permeable to gas and which will not absorb water vapor; those which are impermeable to gas but will absorb water vapor; and, those which are permeable to gas and also absorb water vapor. He also listed temperature as an important factor.

Barrer (1939) tried to find a relationship between the plasticity of a polymer and the diffusion of a gas molecule within it, but could not find such a relationship. He concluded that, "the elasticity which allows gases to diffuse rapidly in rubber is on a molecular scale, and may have its origin in thermal agitation with momentary separation of sections of the polymeric chains."

Dubois and Tressler (1939) stated, "the air in most low temperature storages usually has a low relative humidity due to the condensation of much of its moisture on the coils of the refrigerating system."

Rabak (1940) was of the opinion that proper packaging of frozen fruits and vegetables for consumer use constituted an

important factor in the frozen pack industry, since incorrect packaging may be responsible for serious deterioration in storage. He felt the importance of gas-tight, moisture-proof containers for the prevention of deterioration through dehydration, contamination, and oxidation was well recognized by the industry at that time. Rabak continued that the type of container to be selected for a specific commodity depends upon the nature of the product and the manner of freezing. He defended tin or glass on the basis of their resistance to penetration of moisture vapor and ease of sealing, but stated that paperboard containers offer definite commercial advantages and are, therefore, widely used for packaging frozen fruits and vegetables. He asserted that paperboard cartons supply a package that is distinctive for frozen foods due to light weight, convenient shape, and ability to take rough treatment at low temperatures.

Rabak after experimenting with different cardboards, rated them as follows: coated, impregnated, and untreated in the order of resistance to passage of water. Creasing was found to materially interfere with the efficiency of so-called waxed papers, while moisture-proof viscose and rubber-compound sheets were deemed to be superior to the average treated-paper material. Practical experiments with peas showed the efficiency of packages in preventing moisture-vapor loss in storage depended largely upon the relative moisture-vapor proofness of the liner or wrapper and the efficiency of the seal. Ordinary moisture-vapor proof paper heavily waxed on both sides, moisture-vapor

proof viscose sheets, and rubber compound sheets were all found to be reliably efficient in preventing loss of moisture-vapor during nine months' storage at 15 and 0° F.

Sager (1940) investigated permeability of elastic polymers to hydrogen and found natural rubber, perbunan, neoprene G, vistanex, thiokol Dx, and pliofilm diminished in the order mentioned. He found the increase in rate of permeation with increasing temperature was expotential in all cases. He assumed rate of permeation in mass per unit time as proportional to the partial pressure of the gas and inversely proportional to the thickness of the film.

Southwick (1941) defined a food package as "a protective, low cost, attractive and convenient means of delivering food to the consumer." He also stated that the protective factor covers "prevention of change in state of the package contents as well as giving physical protection." He explained that in many cases, the presence of very little oxygen results in serious flavor changes. In line with this, he believed that deterioration of the product proceeds in proportion to the oxygen transmission value of the material.

Southwick stated,

> Much of the existing confusion and loose claims are the result of the dearth of published data on gas diffusion through thin films, and of the erroneous assumption that physical density and mechanical perfection are all that is necessary.

He also stated that glass or tin will meet all protective demands in a food package, but because of cost, cheaper structures have been developed.

Stevens (1941) listed the principal three agents that tend to lower quality in most frozen food items during freezing and storage as desiccation, oxidation, and autolysis. He continued that to guard the food against contact with air is the only insurance against desiccation and oxidation. Therefore, proper packaging is vital.

Barrer (1941) said, "In materials where very small permeabilities are being encountered, pressure, area of membrane, thickness of membrane, and temperature are possible varisbles in the permeation kinetics." He reported the velocity of diffusion as being inversely proportional to the thickness of the membrane and that a given type of membrane will give somewhat different permeabilities for different specimens.

Diehl and Rabak (1942) listed poor sealing of liners and over-wraps as an inherent weakness of frozen food packaging. In relation to moisture-vapor proof materials they said,

> It will not suffice to assume protection on the basis of tests made at room temperatures. Some materials become brittle and crack or tear easily at temperatures below freezing. The good qualities of packaging materials for protecting foods at temperatures higher than freezing must be regarded as tentative for frozen foods, until actual tests have proved them.

They reported variation between different sheets which have been subjected to similar treatments. Some double paraffin coated sheets proved more efficient than others, even when the thickness of paraffin film was the same. Closely "knit" texture proved more efficient than loosely "knit" texture papers.

Diehl and Rabak also gave evidence of the low relative humidities in low temperature storages, and stressed the need of an effective package barrier in order to prevent passage of moisture from the food to the surrounding atmosphere.

Throckmorton (1943) said,

> There has always been a demand for food packages that would give better protection for about the same cost, or the same relative protection for less cost. Paper, being the cheapest of the various commercial packaging materials, has constantly sought to replace tin, glass, and all the more expensive and more durable substances.

He believed the most universal problem was to resist or delay the transfer of vapors and gases, and that all too frequently such studies are carried out on the material itself without regard to the efficiency of seals and closures. There are many satisfactory materials, he said, but the problem lies in the efficiency of construction on a production basis. Rigid cartons involve the same tight closure problems as film bags, though to a greater degree.

Todd (1944) reported that although the importance of moisture resistance in packaging materials is quite generally recognized, gas permeability seems to have received less attention than it deserves. Oxidative changes in food products often result in rancidity, discoloration, or loss of flavor and nutritive value.

Working with ethyl cellulose, he found the gas transmission rate varied directly with the thickness of the sheet. Higher temperature accelerated gas transmission rate while higher humidity slowed down the rate.

Todd's apparatus was designed to measure transmission of gases through sheets and films, and employed a volumetric principle. Shuman (1944) designed an apparatus which was also used to test sheet materials, but employed a manometric method of determination. Neither of these methods could be applied to the study of a finished container as such.

Smith and Kleiber (1944) described an apparatus for measuring the rate of gas penetration through flexible materials, particularly oxygen penetration into pouches used for food packaging. The principle of this method involved differences in partial pressure, but essentially equal total pressure on both sides of the test membrane. They stated that the absolute accuracy of the measurements is determined mainly by the accuracy of gas analysis while the relative accuracy can be changed by varying the time of penetration of oxygen into the pouch.

Smith and Kleiber also listed the rate of change of partial oxygen pressure in the gas inside a package among the most important criteria for grading a container. And stated, "the rate of penetration by diffusion (dependent on differences of partial pressure only) can be determined by gas analysis or other means designed to measure oxygen concentration."

They calculated the rate of oxygen penetration by assuming that the amount of gas in the diffusion chamber remained constant, and considered the effect of changes in total pressure (barometric fluctuations) negligible compared with the effect of a difference of partial pressure of 0.2 atmosphere. They chose

the diffusion time for each sample so that the change in total amount of gas by oxygen entering the chamber was also negligible.

The formula used by Smith and Kleiber for calculating the rate of oxygen penetration was as follows:

$$\frac{\text{(volume of gas in diffusion chamber \& sack) x (increase } O_2 \text{ concentration)}}{\text{(sack area exposed) x (time)}} =$$

rate/unit area/unit time.

Lahey (1944) concluded that laboratory tests should not be relied upon exclusively for determining the value of a container, but should be used to eliminate the poorest containers, thereby reducing the amount of time to be spent testing containers filled with hygroscopic materials under actual conditions of storage. He thought actual storage tests should include variations in temperature and humidity within each day and from day to day. They should also include handling such as occurs in warehousing, transportation, or any other factors which could alter the permeability of a material.

Davis (1946) stated,

> The need for information on the gas permeability of food packaging materials has been appreciated by many workers, for many foods are subject to deterioration through oxidation by atmospheric oxygen which may permeate into the package through the wrapper.

He agreed with previous work that the principal two mechanisms involved are: (a) Pore permeation which is due to diffusion of the gas through small pores or orifices in the sheet material, and (b) solution permeation, in which the gas dissolves in the

sheet material, diffuses through the sheet, and evaporates from the other side.

While working with sheet materials, Davis found that with non-moisture sensitive sheets, varying the relative humidity between 0 and 75 percent had little or no effect on the gas permeability; however, on those materials which were moisture sensitive, extreme variation was produced. He reported different samples of the same sheet material may show wide variations in permeability.

Regarding the principle used by Smith and Kleiber, Davis said,

> The condition of different partial pressures and equal total pressure on the two sides of the test sheet represents the usual conditions which are encountered with packages made from flexible sheet materials, except where vacuum packaging is used.

In an attempt to get a general picture of the route followed by a gas molecule, the following quotation seemed to sum up the prevalent views. Doty, Aiken, and Mark (1946) said,

> The process of permeation of water through an organic high polymer film is considered to be roughtly as follows:
>
> Water molecules dissolve in the film on the side exposed to vapor, migrate by activated diffusion through the film, and evaporate from the other side. In general, flow occurs through preformed capillaries only as result of mechanical injury or imperfection. An individual water molecule moves about in the film by jumping into holes in the immediate neighborhood; these holes constantly form and disappear as a result of random motion of segments of long chain molecules. Thus, the net effect is a drift to the dry side.

Cartwright (1947) concluded that it is generally necessary in giving gas permeability data to state the temperature and

relative humidity at which they were taken. He made the following comment on the apparatus of Smith and Kleiber,

> Air at atmospheric pressure is in contact with a relatively large area of the sheet material under test, which serves as a portion of the confining walls of a relatively large volume of nitrogen, also at atmospheric pressure.

This allows for an almost equal total pressure of gas on both sides of the specimen, but the partial pressure of oxygen differs by approximately 0.2 atmosphere. Thus atmospheric oxygen diffuses into the nitrogen filled space due to this difference in partial pressure.

Sarge (1947) did some work to find the relationship between molecular weight and the permeability of gases. He found some relation between permeability and molecular diameter, molecular weight and degree of saturation for helium, hydrogen, oxygen, nitrogen, and carbon dioxide. He believed this observation, which was contrary to some earlier work, was due to the inertness or solvent resistance of polymers and copolymers of vinylidine chloride.

Tressler and Evers (1947) reported work by Kertesz showing that the tendency of sliced peaches to discolor varies directly with the amount of catechol-tannin substance present. They also reported work by Cox and MacMasters in 1942, which demonstrated that packing sliced peaches in nitrogen served to retain their color during freezing and storage.

Tressler (1948) listed the cause of discoloration of some fruits as oxidation of easily oxidized components of the fruit

tissue (principally catechol tannins) by oxygen of the air.

Tressler (1948) emphasized that if quality is the sole consideration, either glass or enamel-lined tin containers should be used for fruits, as any type of paperboard carton will permit the passage of some oxygen. However, Gortner, Erdman, and Masterman (1948) said that packaging materials, by excluding or minimizing contact with air, tend to lessen undesirable oxidative reactions.

MATERIALS AND METHODS

Description of Materials

Three types of film liner bags and two regular frozen food cartons were used for the experiments described (Plate VI). In addition, an ice cream carton and a glass beaker were used as controls. Descriptions of these containers follow:

I. Polythene bag - this was a translucent plastic liner bag of 2/3 quart capacity. Specific gravity of the material is 0.92. Brittle temperature is -58° F.

II. MSAT Cellophane liner bag - transparent cellophane bag of 2/3 quart capacity (Specifications unavailable)

III. Laminated carton

Cover

Endboard - bleached kraft board with outside coating of paraffin and inside ply of glassine. Total caliper 0.0275 inch.

Cover ring - two layers of bleached kraft with inside and outside coatings of paraffin.

Can

Sidewall - two layers of bleached kraft. Outside coating of paraffin and an inside ply of glassine.

Bottom - bleached kraft board.- Outside coating of paraffin and an inside ply of #300 MS-1 cellophane.

IV. Ice cream carton control - a common can type ice cream carton with a light layer of wax on the outside.

V. Waxed carton - 2 layers of body stock, basic weight 133 pounds and a caliper of 0.103. The bottom stock has a basic weight of 325 pounds and a caliper of 0.024.

VI. Kraft bag - pint size, bleached and plasticized kraft paper coated with patented microcrystalline wax. Average caliper 0.0045. Total weight 54# per ream on a 34 x 36 500-sheet basis.

VII. Glass beaker control. Ordinary 600 ml Pyrex beaker.

Apparatus and Method of Operation

The experiments were conducted in a frozen food storage room at a temperature which averaged close to 5° F. The relative humidity of this room was about 25 percent which is sufficiently low to avoid any great effect upon the permeability of the materials tested.

The modified Smith and Kleiber apparatus described on page 9 was originally designed to measure the rate of gas penetration through flexible materials, particularly for determining the rate of oxygen penetration into pouches used for food packaging. In the present case, it was also used on some rigid containers, and it appeared to be easier to use on these rigid containers than on the film pouches.

A portable Burrell Gas Analysis Apparatus, cabinet model No. A 39-503, was used to determine the percentage of oxygen in the gas inside the apparatus at the beginning and again at the end of each sample period.

The apparatus (Plates I and II) consisted of the following parts: a gas diffusion chamber, A, (5.2 x 18 cm) having an iron mercury receptacle permanently sealed near the top of the chamber by Dekotinsky wax. This bath was sealed directly to the outside of chamber A, so that the mercury bath would form a seal against the glass, thus insuring an air-tight connection. To the bottom of the diffusion chamber, two attachments of 9 mm (outside diameter) glass tubing were made. Tube B was inserted and sealed so that its top end reached within about 5 cm of the top of the diffusion chamber and was attached to three-way stopcock, C, at its bottom end. Tube L formed a lead from the bottom of the chamber down to three-way stopcock M, in turn connected to 200 milliliter glass bulb, O, and through tube R to three-way stopcock Q. This arrangement allowed the mercury from the leveling bottle, P, to be passed into tube L either through the glass bulb O, or through tube R, by-passing bulb O.

The rigid containers, film bags, or a glass beaker served to close the top opening, G, of chamber A, and an air tight seal was formed by immersing the open end of the container in the mercury bath. Due to the upward pressure exerted upon the container by the specific gravity of the mercury, and by the pressure of the gas being forced through the apparatus, it was found neces-

sary to hold the closing container down in the bath by means of two rods, H, passed across the top of the container and held down by strips of rubber, I. The rubber strips were looped over each end of the rods from a ring beneath the iron receptacle. Thus, a constant tension was exerted holding the container down in the bath. The film bags tested were slipped over a wire frame to keep them distended. The frame also served to submerge the open end of the bags in the mercury bath. A small strip of rubber was placed between the holding rods and these film bags to guard against any possible leaks resulting from tearing.

In operation, a sample carton was placed on the apparatus and secured in the mercury bath, then rubber tubing was connected to a nitrogen cylinder and to tube D below stopcock C. Stopcocks C, M, and N were opened, and a flow of nitrogen allowed to pass through tube B, flushing the air out of the container and chamber A, then passing down through tube L and out through stopcock N, which was extended by means of a rubber hose. The end of the hose dipped into a container of water and a constant bubbling from the end of this tube gave assurance that the nitrogen was passing through the apparatus with a positive pressure at all times.

While the nitrogen was passing along its route, the leveling bottle P, connected to the bottom arm of stopcock Q with rubber, pressure tubing was raised, and the mercury level forced up in bulb O to a point just short of passing into the side-arm leading to stopcock N. The mercury level was then dropped back to level

1, and again raised to the same point to make sure that all air was flushed out of bulb O, and at the same time gave a nearly constant length of time during which the nitrogen flush gas was run through the apparatus for each sample. After returning the mercury to level 1, stopcocks N and C were shut off simultaneously, stopping the flow of nitrogen through the apparatus and forcing it to pass through an escape outlet provided by placing a glass T in the nitrogen line, the side arm of which was extended by rubber tubing so that it also bubbled out through the container of water. This also formed an escape valve to insure against too much pressure inside the apparatus during flushing.

The next step was to obtain an initial sample of the gas in the apparatus to ascertain the percentage of oxygen present at the beginning of the sampling period. To do this, a gas sampling bulb, E, of 250 ml capacity was attached to tube D by means of a short length of rubber tubing which was left permanently attached to the sampling bulb but was slipped on and off of tube D, or the intake capillary of the Burrell gas analysis apparatus (Plates II and III). By turning stopcock C to connect tube D with the air outlet above stopcock C, then raising mercury leveling bulb F, the air was forced from the sampling bulb and as soon as the mercury level passed into the outlet tube, stopcock C was closed and the leveling bulb F was lowered to a point where all the mercury could flow out of the sampling bulb. The leveling bottle P, was then raised to a height where the mercury from it could flow from level 1, through bulb O to

level 2. By simultaneously manipulating stopcocks Q and C, the volume of gas held in bulb O was displaced into the sampling bulb. After closing both stopcocks on the sampling bulb and also stopcocks C and M, the sampling bulb was removed.

Since the weight of the mercury was found to be too much to leave resting against stopcock Q for any extended period of time, stopcock M was closed, leaving a small column of mercury, as a seal, between it and level 2. By lowering leveling bulb P and opening stopcock N to the atmosphere, the mercury in bulb O could be returned to level 1.

The sampling bulb and its leveling bulb were used as a unit, and were left permanently connected by rubber, pressure tubing. The metal frame shown in Plate III was used to transport them in and out of the freezer room and to hold them in position for analyzing the gas sample. Since the tests were run in a plate freeze room at an average temperature of about 5° above 0, Fahrenheit (Fig. 1), it was thought desirable to let the sample come to room temperature before continuing with the analysis. A minimum time of one and one-half hours was allowed after each sample was drawn for this equalization of temperatures to occur. A water-bath surrounding the burette on the analysis apparatus prevented any excessive temperature change during the time required for actual analysis.

The analysis was run by connecting the sampling bulb, E, to the analysis apparatus as shown in Plate III. Then about 30 milliliters of the sample were drawn into the burette in order to

clear the capillaries of any gas present when the connection between the sampling bulb and the apparatus was made. This was passed into the first contact pipette, containing potassium hydroxide, by raising the small leveling bottle containing an aqueous salt solution until this solution stopped just at the top of the burette. The gas was left in contact with the alkaline solution for approximately one minute before it was returned to the burette, care being taken to stop the potassium hydroxide level at the starting point in the capillary tubing. This operation was repeated a second time, although the Burrell manual states that the carbon dioxide need not be removed, as normal air does not contain enough to be significant in an ordinary analysis. It was felt that this insured against any error in the oxygen absorption reading due to any CO_2 which might be present.

The gas was then passed into the second pipette containing alkaline pyrogallic acid, which absorbed any oxygen present. When a constant reading had been obtained on successive runs, the remaining gas was exhausted through the left side of the manifold, since any gas which would interfere with the accuracy of the analysis had now been absorbed.

The actual sample was then taken and as near 100 ml volume as possible was taken into the burette. The large sample minimized any common analytical errors which are inherent in such a procedure. The burette was graduated by 0.2 ml divisions, therefore, could be read by estimation to 0.1 ml.

The same procedure was followed as before, passing the gas

first into the potassium hydroxide pipette to absorb any carbon dioxide, then into the alkaline pyrogallic acid pipette to absorb the oxygen. In each case, the difference between the beginning reading and the end reading on either pipette gave the milliliters absorbed in that pipette, and served as a basis for obtaining the volume percentage of carbon dioxide or oxygen present.

At the end of the sample period (determined by the permeability of the material being tested), the second gas sample was taken. This was accomplished by connecting the gas sampling bulb E as before, then raising leveling bottle P to a point where its mercury level was approximately even with the top of the diffusion chamber. Stopcocks M and Q were adjusted so that the mercury flowed through tube R into tube L and on up into the diffusion chamber, A, to level 3. The mercury level in the sampling bulb was lowered simultaneously as before, causing the gas to flow into the sampling bulb. The mercury in the diffusion chamber was then returned to the leveling bottle and the sampling bulb removed for analysis.

Calculations

In the present experiment, it was not possible to keep the oxygen concentration in the diffusion chamber from reaching saturation in all cases. For the cartons on which this was true, the gas was obviously coming in around the lids. With the other containers, it was possible to obtain a measure of the diffusion rate since a concentration less than that of air could be ob-

tained for the sample periods run.

A measure of the comparability of separate samples of gas taken from the diffusion chamber was obtained by comparing the beginning concentration of oxygen at the beginning of each control period, using the glass beaker. These values are shown in the table below.

#1 (percent)	#2 (percent)	Elapsed time in hours	Increase in O_2 (percent)
0.0	1.7	24.0	1.7
0.3	1.5	12.5	1.2
0.6	1.5	24.0	0.9
0.1	4.0	73.0	3.9
0.0	2.0	25.0	2.0

Comparison of the first set of samples with the second set (#1 and #2) also gives an idea of how much leakage could be expected in the apparatus.

In order to figure the rate of penetration on a comparable basis, it was necessary to know the volumes involved. The diffusion chamber was filled with water, level with the top, and measured down to level 2. Then after each container was tested, the volume of that container was obtained by filling the container with water to the point reached by the mercury bath. The sum of the volumes of the diffusion chamber and the container gave the total volume of gas into which the oxygen could diffuse. The areas were figured according to the shape of the container, with the closed end of the film bags being considered as a rectangle, since no satisfactory method could be devised to allow for the folds caused by the rods used to hold the bags down in

the mercury bath.

The calculations were made according to the following formula:

$$\frac{\text{Volume of gas in diffusion chamber and sack}}{\text{Sack or container area exposed to air}} \times \frac{\text{Increase in } O_2 \text{ concentration}}{\text{Time}} = \text{rate/unit/unit area/ time}$$

Example, from kraft bag:

$$\frac{(295 + 670)\ 0.177}{394.7 \times 12.5} = 0.0346 \text{ ml/sq cm/hr.}$$

In the course of running the experiment, it soon became evident that the rate of oxygen penetration into all three rigid cartons being tested was far too rapid to be due to diffusion alone. The course of the experiment was changed somewhat from the original plan, therefore, in an attempt to find whether sealing the lids of these containers with a mixture of bees-wax, paraffin, and vaseline (such as is used on moisture-vapor determinations) would cause a significant difference in the amount of time required for the oxygen concentration to reach the same percentage. It was believed that this constituted the weak point in these containers, as preliminary runs at room temperature had failed to reveal any such rapid penetration of oxygen when the factory sealed ends of these same containers had been tested.

DISCUSSION

An idea of the oxygen concentration values at the beginning and end of each sample period can be obtained by referring to Table 2. It is also possible to obtain a general comparison of the different containers tested. A comparison of the oxygen percentages between containers is not directly comparable since different volumes and areas are involved for each container. However, some idea can be obtained from such an examination.

By studying the column entitled "concentration sample #1," the defective hand-made seals on the containers are revealed. The Polythene bag, the cellophane bag, the kraft bag, and the glass beaker all show oxygen concentrations inside the apparatus which average 0.22 percent or less. The waxed carton averages 0.74 percent, while the laminated carton and the ice cream carton average 2.08 percent and 7.72 percent respectively. When it is considered that these original gas samples were taken less than five minutes after the nitrogen flush gas was run, it becomes apparent that something has happened in the laminated carton and the ice cream carton. Either gas has leaked in around the lids, or the nitrogen flush gas was unsuccessful in carrying the oxygen out of the apparatus. Although this latter possibility should be considered, the fact that all samples were flushed with nitrogen for about the same length of time, and the fact that the volumes involved were smaller for the two containers showing the highest oxygen values, should also be considered (See Table 1 for a comparison of volumes and areas involved).

To the author, this indicated that the lids on the ice cream carton control and on the laminated carton were allowing oxygen to enter, and possibly the lid of the waxed carton also. To further substantiate this possibility, the slight vacuum drawn upon the apparatus in taking the gas samples caused no change in the level of mercury in the mercury bath.

This vacuum was only a temporary condition caused by the mercury receding from the gas sampling bulb into leveling bulb F at a faster rate than the mercury level could rise in bulb O from leveling bulb P. When a sample was being taken on the glass beaker control, the vacuum would cause the mercury level to rise inside the beaker and fall on the outside of the beaker. On the waxed carton, the level could be observed falling on the outside, and on the film bags, the sides would deflate, then as the other mercury level caught up, they would swell out again. These indications were used as a guide for manipulating stopcocks C and Q. If stopcock C was not shut off in order to let the left-hand mercury level catch up, mercury from the bath would be drawn over the edge of chamber A and would fall down inside the apparatus. With the two cartons which did not appear to hold against the vacuum, both stopcocks could be opened with no apparent effect on the mercury level in the bath. Therefore, air must have been entering to equalize the pressures.

The concentrations shown for the end of the test period when contrasted with those for the beginning of the period give a still better idea of what has happened. The Polythene and cel-

lophane bags still have rather low values, comparable to the values shown for the glass beaker control. The kraft bag, however, has a final concentration which approaches the concentration of oxygen in the air, or 20 to 21 percent. The same high end concentrations are seen for the laminated carton and the ice cream carton, with a somewhat lower set of values for the waxed carton.

The "hours run" column adds weight to the above information. The Polythene and cellophane bags, run for periods of about 12 hours, show no more increase of oxygen than does the glass beaker. The kraft bag, although it did not appear to allow gas to pass through the sealed end, has a final oxygen concentration approaching that of the air. This would indicate that oxygen has diffused through the material or the seal at a rather steady rate. The three cartons all run for relatively short periods of time, show values approaching that of air. This shows that oxygen could enter these cartons at a very rapid rate.

Table 3 shows values of a more comparable nature, derived from the data collected in Table 1. These values take into consideration the differences in volume and area between the various containers, and are expressed as: ml of gas/sq cm/hour. These units are comparable for all containers and were obtained by use of the formula given in the Materials and Methods section.

A statistical analysis of these data (Table 4) shows extreme significance between cartons. The array of carton means (Table 5) shows that the cellophane bag, the glass beaker, and

the Polythene bag are not significantly different from one another. The differences shown are within experimental error. The kraft bag approaches significance, and all three rigid cartons are significantly different from the film bags and the glass beaker.

Table 6 shows an accumulation of data on the three rigid cartons of Table 1, plus another set of replications for the same three cartons tested with the lids sealed. Table 7 records an extraction of oxygen concentration values and hours run shown in Table 6. First, comparing the original concentration values for the lids unsealed with the lids sealed, a lower average concentration is found for the original samples in the sealed treatment than in the unsealed treatment. This is true for all three cartons. A lower end concentration is seen for the laminated carton when sealed compared to the unsealed, both treatments tested for a similar length of time. The same thing is true for the waxed carton, but the ice cream carton shows almost the same values for a similar series of test times on both the sealed and the unsealed treatments. This may have been due to the fact that the pint containers which were used in the first series of replications could not be obtained for the second series, therefore, quart size containers were used, and the additional area may have offset any effect obtained by sealing the lids.

Examining Table 8, the values for the laminated carton show consistently lower penetration in the sealed treatment. This would indicate that sealing the lids did slow the rate of oxygen

penetration. The sealed values for the ice cream carton appear to be larger over all than the unsealed values, probably due to the change to a larger container for the sealed treatment. The values for the waxed carton, follow the lead established for the laminated carton, the sealed values being smaller in all cases.

Following up with a statistical analysis of these values as shown in Table 9, significant differences between cartons are indicated at the 1 percent level, but not at the 5 percent level of probability. The array of carton means (Table 10) shows the values for all but the sealed waxed carton to be significant, though in order of rank, only the ice cream carton failed to give a lower value for the sealed as compared to the unsealed mean for the same carton.

Table 11 shows data for a series of only one replication for each carton. This series was run with the factory sealed ends up for test, and the open ends submerged in the mercury bath. Since only one series of this treatment was completed, a statistical analysis could not be made.

In Table 13 where the value obtained for the beginning concentration in Table 11 is compared with the average beginning value in Table 2, the Polythene and cellophane bags are almost the same in both tests. For the laminated carton, and the ice cream carton, the beginning concentrations are smaller for the factory sealed end. The waxed carton beginning concentration is somewhat smaller, but no significant difference can be observed for the kraft bag. The end concentration is smaller for the

Polythene bag, but larger for the cellophane bag, when the factory-sealed end and the hand-sealed end are compared in the last two columns of Table 13. The factory end shows a much smaller value than the lid for the laminated carton. The ice cream carton and kraft bag show almost the same values either way. The factory end of the waxed carton shows a much smaller value than for the lid. Reference to Table 12 will reveal that the three bags were tested for about the same amount of time in both tests, but the cartons were tested for longer periods on the factory end than for the lids. The laminated carton and the waxed carton still showed much lower values for the end concentration than they did in Table 2. This would tend to show that the factory-sealed end was more efficient than the cap lid on these cartons. More replications need to be run before this conclusion can be made definitely.

Table 1. Oxygen concentration data obtained from five replications on each container. The factory-sealed end of the film bag or container was placed on the diffusion chamber so that the laboratory seal of the film bags or the lid of the rigid containers was tested as an oxygen barrier.

Container	Series	Concentration, sample #1	Concentration, end of period	Increase in O_2 concentration	Volume of container in ml	Area of container in sq cm	Hours run	Average temperature in °F.
		Percent						
Polythene bag, 2/3 quart	B	0.1	1.0	0.9	1200	512.1	12.50	4.5
	C	0.6	7.4	6.8	1200	512.1	12.50	3.9
	D	0.2	1.2	1.0	1130	526.7	11.00	3.8
	E	0.0	0.6	0.6	1100	541.3	12.50	4.2
	F	0.2	1.1	0.9	1120	558.1	12.75	4.8
MSAT Cellophane bag, 2/3 quart	B	0.2	1.0	0.8	740	372.9	12.00	4.4
	C	0.2	0.6	0.4	710	387.3	12.25	8.1
	D	0.2	1.0	0.8	700	372.9	12.00	4.8
	E	0.2	0.8	0.6	735	387.3	12.33	4.8
	F	0.2	0.6	0.4	690	424.8	17.50	4.7
Laminated carton, 1 pint, can-shaped	B	3.1	20.2	17.1	450	250.7	10.00	5.2
	C	2.2	19.8	17.6	460	261.2	2.50	4.5
	D	1.5	19.6	18.1	478	261.2	2.67	4.7
	E	2.0	19.0	17.0	500	261.2	2.25	4.8
	F	1.6	19.2	17.6	460	250.7	2.00	6.0
Ice cream carton, control, can-shaped	B	9.2	20.0	10.8	460	255.9	2.50	4.5
	C	10.4	20.2	9.8	455	255.9	2.00	5.0
	D	7.3	20.2	12.9	460	258.6	2.50	3.7
	E	5.6	20.2	14.6	470	261.2	2.67	4.8
	F	6.1	20.0	13.9	490	261.2	2.17	4.8
Waxed carton, 1 pint, tub-shaped	B	0.8	5.6	4.8	470	270.8	3.00	5.7
	C	1.6	13.4	11.8	480	280.4	3.25	4.5
	D	0.6	7.8	7.2	485	277.2	2.33	4.0
	E	0.3	10.0	9.7	485	280.4	3.25	3.2
	F	0.4	13.4	13.0	470	280.4	4.25	5.4
Kraft bag, 1 pint	B	0.2	17.9	17.7	670	394.7	12.50	4.4
	C	0.2	19.3	19.1	660	388.6	12.00	4.8
	D	0.0	19.9	19.9	685	394.7	12.00	4.8
	E	0.2	15.6	15.4	700	434.5	12.25	3.7
	F	0.3	16.8	16.5	720	419.2	12.67	4.3
Glass beaker, control, 600 ml	B	0.0	1.7	1.7	600	352.9	24.00	3.3
	C	0.3	1.5	1.2	600	352.9	12.50	4.7
	D	0.6	1.5	0.9	600	352.9	24.00	8.4
	E	0.1	4.0	3.9	600	352.9	73.00	7.4
	F	0.0	2.0	2.0	600	352.9	25.00	6.1

Table 2. Oxygen concentration data summarized from Table 1.

Container	Concentration sample #1	Average beginning concentration	Concentration end of period	Average end concentration	Hours run
	Percent				
Polythene bag, 2/3 quart	0.1		1.0		12.50
	0.6		7.4		12.50
	0.2	0.22	1.2	2.26	11.00
	0.0		0.6		12.50
	0.2		1.1		12.75
MSAT Cellophane bag, 2/3 quart	0.2		1.0		12.00
	0.2		0.6		12.25
	0.2	0.20	1.0	0.80	12.00
	0.2		0.8		12.33
	0.2		0.6		17.50
Laminated carton, 1 pint, can-shaped	3.1		20.2		10.00
	2.2		19.8		2.50
	1.5	2.08	19.6	19.6	2.67
	2.0		19.0		2.25
	1.6		19.2		2.00
Ice cream carton, control, can-shaped	9.2		20.0		2.50
	10.4		20.2		2.00
	7.3	7.72	20.2	20.0	2.50
	5.6		20.2		2.67
	6.1		20.0		2.17
Waxed carton, 1 pint, tub-shaped	0.8		5.6		3.00
	1.6		13.4		3.25
	0.6	0.74	7.8	10.2	2.33
	0.3		10.0		3.25
	0.4		13.4		4.25
Kraft bag, 1 pint	0.2		17.9		12.50
	0.2		19.3		12.00
	0.0	0.18	19.9	17.8	12.00
	0.2		15.6		12.25
	0.3		16.8		12.67
Glass beaker, control, 600 ml	0.0		1.7		24.00
	0.3		1.5		12.50
	0.6	0.20	1.5	2.0	24.00
	0.1		4.0		73.00
	0.0		2.0		25.00

Table 3. The following table shows values for five containers and two controls for five replications. The diffusion values are expressed as: ml of gas/sq cm/hour. These values were calculated from data in Table 1.

Series	Polythene liner bag, 2/3 quart	MSAT cellophane liner bag, 2/3 qt.	Laminated carton, 1 pint, can-shaped	Ice cream carton, control, can-shaped	Waxed carton, 1 pint, tub-shaped	Kraft bag, 1 pint	Glass beaker, control, 600 ml
B	0.00209	0.00185	0.0508	0.127	0.0451	0.0346	0.00180
C	0.0159	0.000847	0.203	0.144	0.100	0.0391	0.00242
D	0.00247	0.00178	0.201	0.151	0.0870	0.0412	0.0009
E	0.0124	0.00129	0.230	0.160	0.0831	0.0288	0.00135
F	0.00178	0.000530	0.265	0.192	0.0834	0.0315	0.00203

Table 4. Analysis of variance on data in Table 3.

Sources of variation	D/F	Sums of squares	Mean square	F	P
Cartons	6	181,028.50	30,171.00	31.57	$n_1=6$ $n_2=24$ $\ll .001$
Replications	4	8,245.41	2,061.40	2.16	$n_1=4$ $n_2=24$ $\rangle .05$
Error	24	22,937.83	955.74		
Total	34	212,211.74			

Table 5. Array of carton means.

Cartons in order of value as O_2 barrier	Mean	
MSAT cellophane bag	0.00126	
Glass beaker control	0.00170	
Polythene bag	0.00693	
Kraft bag	0.03504	
Waxed carton	0.07974	*at 5 percent
Ice cream carton	0.15480	**past 1 percent
Laminated carton	0.18996	

* lsd 0.04035 significant at 5 percent level
** lsd 0.05468 significant at 1 percent level.

Table 6. Data obtained from five replications for three cartons with lids unsealed compared with five replications for the same cartons with lids sealed with wax at the juncture with the container.

Container	Series	Concentration, sample #1	Concentration, end of period	Increase in O_2 concentration	Volume of container in ml	Area of carton in sq cm	Hours run	Average temperature °F.
		Percent						
Lids unsealed								
Laminated carton, 1 pint, can-shaped	B	3.1	20.2	17.1	450	250.7	10.00	5.2
	C	2.2	19.8	17.6	460	261.2	2.50	4.5
	D	1.5	19.6	18.1	478	261.2	2.67	4.7
	E	2.0	19.0	17.0	500	261.2	2.25	4.8
	F	1.6	19.2	17.6	460	250.7	2.00	6.0
Ice cream carton, control, can-shaped	B	9.2	20.0	10.8	460	255.9	2.50	4.5
	C	10.4	20.2	9.8	455	255.9	2.00	5.0
	D	7.3	20.2	12.9	460	258.6	2.50	3.7
	E	5.6	20.2	14.6	470	261.2	2.67	4.8
	F	6.1	20.0	13.9	490	261.2	2.17	4.8
Waxed carton, 1 pint, tub-shaped	B	0.8	5.6	4.8	470	270.8	3.0	5.7
	C	1.6	13.4	11.8	480	280.4	3.25	4.5
	D	0.6	7.8	7.2	485	277.2	2.33	4.0
	E	0.3	10.0	9.7	485	280.4	3.25	3.2
	F	0.4	13.4	13.0	470	280.4	4.25	5.4
Lids sealed with wax								
Laminated carton, 1 pint, can-shaped	H	1.3	20.2	18.9	460	263.9	6.50	6.6
	I	0.5	13.2	12.7	465	269.1	2.00	5.6
	J	0.4	14.5	14.1	465	279.7	2.75	4.3
	K	0.4	9.6	9.2	470	274.4	1.59	2.5
	L	4.1	14.0	9.9	462	274.4	2.17	3.6
Ice cream carton, control, can-shaped	H	5.7	20.0	14.3	947	472.4	2.33	6.1
	I	3.9	20.3	16.4	930	477.7	3.00	4.8
	J	3.5	19.8	16.3	940	488.3	2.00	4.7
	K	2.5	19.8	17.3	975	490.9	2.00	3.5
	L	4.1	20.0	15.9	936	485.6	2.00	4.3
Waxed carton, 1 pint, tub-shaped	H	0.0	2.5	2.5	520	280.4	4.50	8.1
	I	0.0	4.1	4.1	510	283.6	8.67	6.8
	J	0.2	4.6	4.4	500	286.8	9.00	2.7
	K	0.3	2.4	2.1	500	286.8	4.00	1.0
	L	0.3	10.1	9.8	510	286.8	11.25	1.8

Table 7. Oxygen concentration data summarized from Table 6.

Container	Concentration sample #1	Average beginning concentration	Concentration end of period	Average end concentration	Hours run
		Percent			
Lids unsealed					
Laminated carton, 1 pint, can-shaped	3.1		20.2		10.00
	2.2		19.8		2.50
	1.5	2.08	19.6	19.6	2.67
	2.0		19.0		2.25
	1.6		19.2		2.00
Ice cream carton, control, can-shaped	9.2		20.0		2.50
	10.4		20.2		2.00
	7.3	7.72	20.2	20.1	2.50
	5.6		20.2		2.67
	6.1		20.0		2.17
Waxed carton, 1 pint, tub-shaped	0.8		5.6		3.00
	1.6		13.4		3.25
	0.6	0.74	7.8	10.4	2.33
	0.3		10.0		3.25
	0.4		13.4		4.25
Lids sealed with wax					
Laminated carton, 1 pint, can-shaped	1.3		20.2		6.50
	0.5		13.2		2.00
	0.4	1.34	14.5	14.3	2.75
	0.4		9.6		1.59
	4.1		14.0		2.17
Ice cream carton, control, can-shaped	5.7		20.0		2.33
	3.9		20.3		3.00
	3.5	3.94	19.8	20.0	2.00
	2.5		19.8		2.00
	4.1		20.0		2.00
Waxed carton, 1 pint, tub-shaped	0.0		2.5		4.50
	0.0		4.1		8.67
	0.2	0.16	4.6	4.74	9.00
	0.3		2.4		4.00
	0.3		10.1		11.25

Table 8. Values for three cartons, each receiving two treatments for five replications. The diffusion values are given as: ml of gas/sq cm/hour.

Series	Laminated carton, 1 pint, can-shaped		Ice cream carton, control, can-shaped		Waxed carton, 1 pint, tub-shaped	
	Unsealed	Sealed	Unsealed	Sealed	Unsealed	Sealed
B & H	0.0508	0.0832	0.127	0.151	0.0451	0.0161
C & I	0.203	0.179	0.144	0.140	0.100	0.0134
D & J	0.201	0.139	0.151	0.206	0.0870	0.0136
E & K	0.230	0.161	0.160	0.224	0.0831	0.0146
F & L	0.265	0.126	0.192	0.202	0.0834	0.0244

Table 9. Analysis of variance on data in Table 8.

Sources of variation	D/F	Sums of squares	Mean square	F	P
Cartons	5	114,319.31	22,863.9	19.82	$<.01$ $n_1=5$ $n_2=20$
Replications	4	18,102.22	4,525.6	3.92	$>.05$ $n_1=4$ $n_2=20$
Error	20	23,072.76	1,153.6		
Total	29	155,494.29			

Table 10. Array of carton means.

Cartons in order of value as O_2 barrier	Mean	
Waxed carton, sealed	0.01642	{* at 5 percent &
Waxed carton, unsealed	0.07972	{** at 1 percent
Laminated carton, sealed	0.13764	
Ice cream carton, unsealed	0.15480	
Ice cream carton, sealed	0.18660	
Laminated carton, unsealed	0.18996	

* lsd 0.04481 significant at 5 percent level
** lsd 0.06100 significant at 1 percent level.

Table 11. Data obtained from a series run with the open ends placed on diffusion chamber and factory-sealed ends up.

Container	Series	Concentration, sample #1	Concentration, end of period	Increase in O_2 concentration	Volume of container in ml	Area of container in sq cm	Hours run	Average temperature in °F.
		Percent						
Polythene bag, 2/3 quart	G	0.1	0.8	0.7	1100	541.3	13.50	6.2
MSAT Cellophane bag, 2/3 quart	G	0.3	1.4	1.1	690	419.0	24.00	4.4
Laminated carton, 1 pint, can-shaped	G	0.6	2.4	1.8	410	261.2	5.00	-1.5
Ice cream carton, control, can-shaped	G	1.1	19.5	18.4	900	483.0	12.10	4.3
Waxed carton, 1 pint, tub-shaped	G	0.2	1.8	1.6	440	267.6	24.00	5.2
Kraft bag, 1 pint	G	0.2	19.1	18.9	710	416.2	12.25	5.2

Table 12. Oxygen concentration data summarized from Table 11.

Container	Concentration sample #1	Concentration end of period	Hours run
	Percent		
Polythene bag, 2/3 quart	0.1	0.8	13.50
MSAT Cellophane bag, 2/3 quart	0.3	1.4	24.00
Laminated carton, 1 pint, can-shaped	0.6	2.4	5.00
Ice cream carton, control, can-shaped	1.1	19.5	12.10
Waxed carton, 1 pint, tub-shaped	0.2	1.8	24.00
Kraft bag, 1 pint	0.2	19.1	12.25

Table 13. Oxygen concentration data summarized from Tables 1 and 11.

Container	Concentration, sample #1 from Table 11	Average concentration, sample #1 from Table 2	Concentration, end of period from Table 11	Average concentration values at end of period from Table 2
	Percent			
Polythene bag, 2/3 quart	0.1	0.2	0.8	2.26
MSAT Cellophane bag, 2/3 quart	0.3	0.2	1.4	0.80
Laminated carton, 1 pint, can-shaped	0.6	2.08	2.4	19.6
Ice cream carton, control, can-shaped	1.1	7.72	19.5	20.0
Waxed carton, 1 pint, tub-shaped	0.2	0.74	1.8	10.2
Kraft bag, 1 pint	0.2	0.18	19.1	17.8
Glass beaker, control, 600 ml		0.20		2.0

CONCLUSIONS

It was concluded that a significant difference exists between the cartons tested, as far as their value as a barrier to oxygen penetration is concerned.

The Polythene and cellophane bags approached a glass beaker as oxygen barriers under the test conditions described. The heat-seal obtained by using a hot iron on the film bags resulted in a more nearly gas-resistant container than was formed by placing the lids on the rigid containers. It was also concluded that with a properly sealed lid, the two rigid type containers, designed for frozen foods, would become better packaging mediums. However, this would not markedly improve the value of the ice cream carton. The kraft bag did not appear to be an efficient oxygen barrier. It is believed that a test of the basic sheet material would not prove as efficient for the kraft bag as for either the waxed or the laminated basic materials. This conclusion was reached by comparing the increase in oxygen concentration for the waxed carton, the laminated carton, and the kraft bag in Tables 2 and 12. These data would tend to show that these two cartons form a much better oxygen barrier at their factory-sealed ends than in the lids, while the kraft bag appeared to have about the same values either way, indicating that the gas was diffusing through the material rather than through the sealed end, or else heat sealing of the material is not satisfactory.

In the present instance, at least, the waxed carton appeared to be more efficient over all than did the laminated carton. The basic material in either of these two containers appeared to be more efficient than that of the ice cream carton. It would appear that both the material and the method of construction enter into the development of a container which is resistant to oxygen penetration.

It is believed that such analytical tests as have been carried out in this experiment should not be relied upon exclusively in rating a frozen food container. On the contrary, such tests should be used only to select those containers which are most likely to appear effective under actual conditions of handling and storage, thus eliminating excessive time spent testing poor containers. Actual tests with hygroscopic materials should be made to supplement these studies.

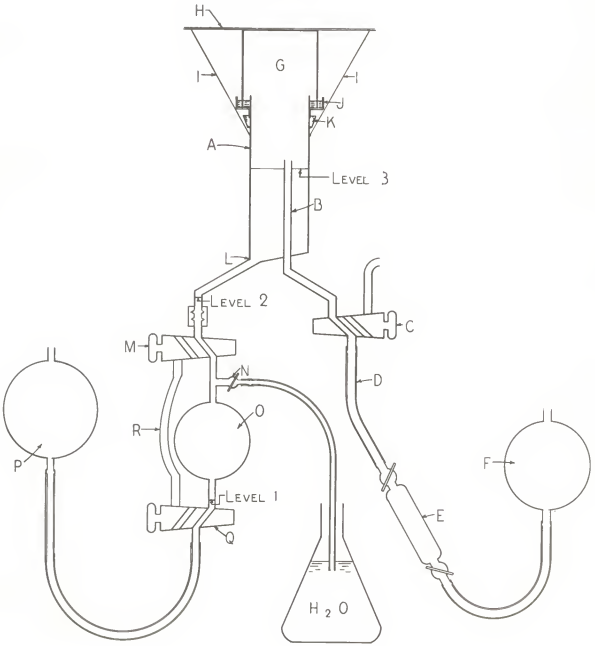
EXPLANATION OF PLATE I

Diagram of diffusion apparatus

A. Gas diffusion chamber.
B. Intake tube for nitrogen flush gas and outlet tube for obtaining gas samples.
C. Three-way stopcock leading to tubes B and D or to the air outlet.
D. Tube to which nitrogen tank or gas sampling bulb was connected.
E. Gas sampling bulb.
F. Mercury leveling bulb.
G. Open end of diffusion chamber A closed by a container.
H. Wire rods used to hold container in the mercury bath.
I. Rubber strips exerting tension downward on end of retaining rods.
J. Mercury receptacle.
K. Ring to which rubber strips were attached.
L. Tube leading to leveling bulb P through bulb O or tube R.
M. Three-way stopcock controlling flow of gas or mercury into tube R or bulb O.
N. Stopcock on nitrogen flush gas outlet.
O. Glass bulb serving as container for original gas sample.
P. Mercury leveling bulb used to control flow of gas in left side of apparatus.
Q. Three-way stopcock controlling flow of mercury at bottom end of bulb O and tube R.
R. Tube allowing mercury to by-pass tube O in forcing second sample of gas into the sampling bulb.

(See Plate II for corresponding photograph)

PLATE I

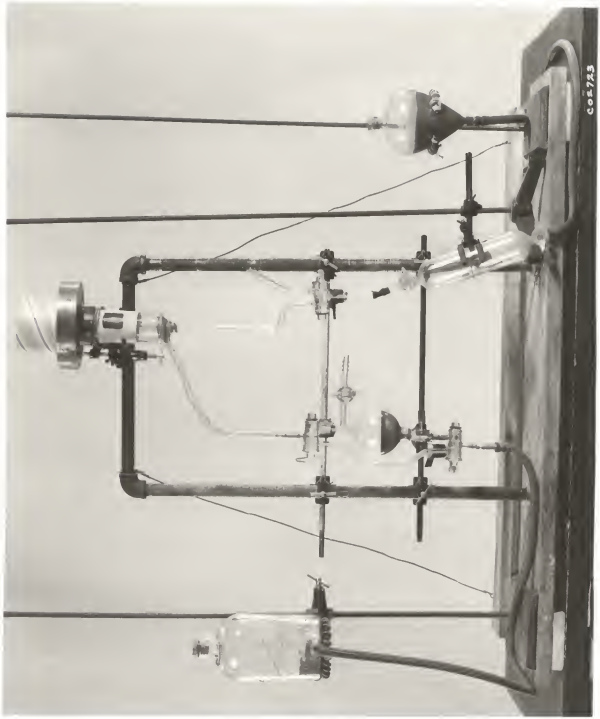


EXPLANATION OF PLATE II

Photograph of diffusion apparatus with gas sampling bulb attached

(See Plate I for labeled diagram)

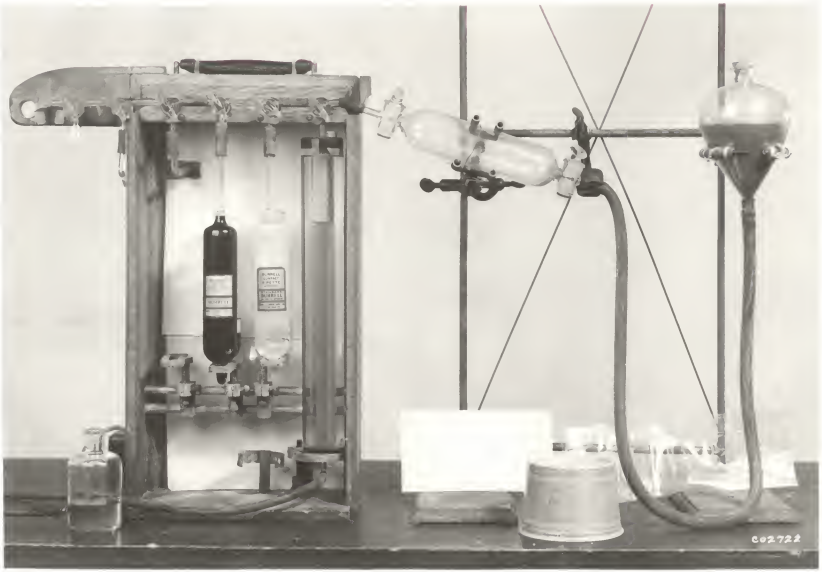
PLATE II



EXPLANATION OF PLATE III

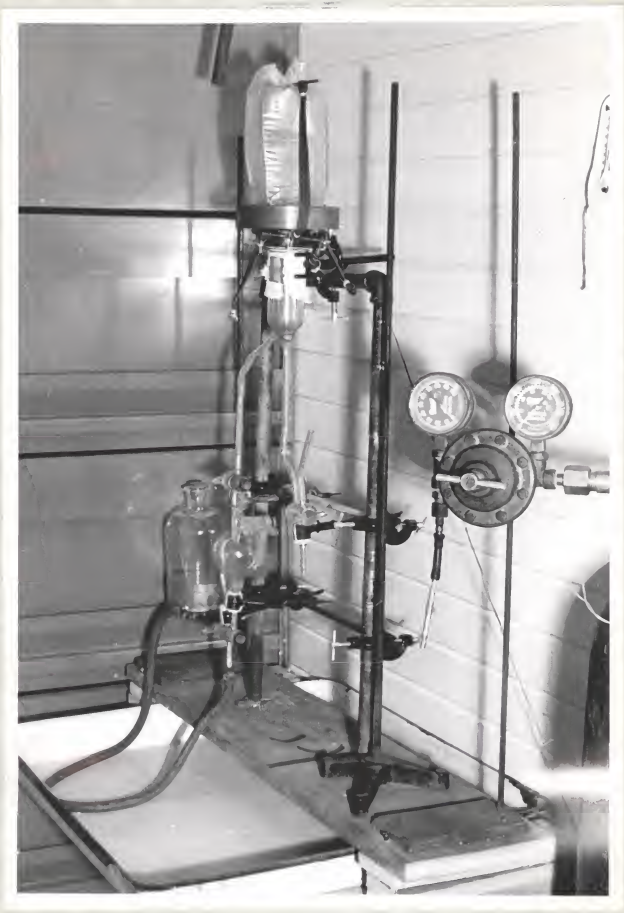
Gas sampling bulb attached to gas analysis apparatus. Three of the containers tested at lower right.

PLATE III



EXPLANATION OF PLATE IV

Photograph of diffusion apparatus and nitrogen tank as set up in freezer room.



EXPLANATION OF PLATE V

Containers and controls used in the experiment

A. Polythene bag
B. MSAT cellophane bag
C. Laminated carton
D. Ice cream carton
E. Waxed carton
F. Kraft bag
G. Glass beaker.

PLATE V

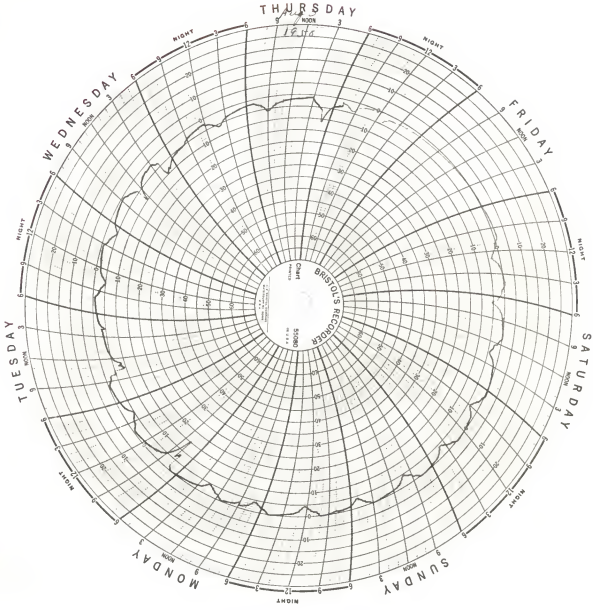


Fig. 1. Copy of recording thermograph kept during the experiment.

ACKNOWLEDGMENT

Sincere appreciation is offered to Dr. G. A. Filinger for suggesting a problem that has never lost its challenge, and for his patient and able assistance at all times. Assistance in obtaining supplies and equipment given by Dr. William F. Pickett, Dr. C. W. Colver, and Dr. A. B. Cardwell made the practical conduction of the experiment possible. The advice and help of Dr. R. H. McFarland in blowing glass for the construction of apparatus were invaluable. Dr. G. W. Leonard aided in gaining an understanding of gas analysis, and Dr. H. C. Fryer's outline of analysis of variance together with assistance of Dr. C. C. Singletary in interpreting results, helped materially in completion of the statistical analysis.

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A STUDY OF OXYGEN DIFFUSION THROUGH FROZEN FOOD PACKAGING MATERIALS

by

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AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Horticulture

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1951

PURPOSE

The main purpose of this study was to determine whether there was a difference in oxygen diffusion rates through some of the available frozen food containers. A second purpose arose as the experiment progressed, and that was to see if sealing the lids of rigid containers with wax would decrease the rate of oxygen penetration into those containers.

METHODS

Three types of film liner bags and two regular frozen food cartons were used for the experiments. In addition, an ice cream carton and a glass beaker were used as controls. Descriptions of these containers follow:

I. Polythene bag - this was a translucent plastic liner bag of 2/3 quart capacity. Specific gravity of the material is 0.92. Brittle temperature is -58° F.

II. MSAT Cellophane liner bag - transparent cellophane bag of 2/3 quart capacity (Specifications unavailable).

III. Laminated carton

Cover

Endboard - bleached kraft board with outside coating of paraffin and inside ply of glassine. Total caliper 0.0275 inch.

Cover ring - two layers of bleached kraft with inside and outside coatings of paraffin.

Can

Sidewall - two layers of bleached kraft. Outside coating of paraffin and an inside ply of glassine.

Bottom - bleached kraft board. Outside coating of paraffin and an inside ply of #300 MS-1 cellophane.

IV. Ice cream carton control - a common can type ice cream carton with a light layer of wax on the outside.

V. Waxed carton - 2 layers of body stock, basic weight 133 pounds and a caliper of 0.103. The bottom stock has a basic weight of 325 pounds and a caliper of 0.024.

VI. Kraft bag - pint size, bleached and plasticized kraft paper coated with patented microcrystalline wax. Average caliper 0.0045. Total weight 54# per ream on a 34 x 56 500 sheet basis.

VII. Glass beaker control. Ordinary 600 ml Pyrex beaker. (No lid)

The experiments were conducted in a frozen food storage room at a temperature which averaged close to 5° F. The relative humidity of this room was 25 per cent which seems sufficiently low to avoid any great effect upon the permeability of the materials tested.

Two pieces of apparatus were used in the experiment. The diffusion samples were obtained by using an apparatus which established equal total pressures, but different partial oxygen pressures on the two sides of the test membrane. By using a nitrogen flush gas to displace the oxygen contained in the container and in the diffusion chamber at the beginning of the sampling period, a condition of very low oxygen concentration could be established. On the outside of the container, however, the oxygen concentration of the air amounted to about 0.2 atmospheric pressure. This simulated the con-

ditions found in a food package as nearly as possible without having an actual food product in the package.

The gas samples were analyzed with a portable Burrell Gas Analysis Apparatus, cabinet model No. A 39-503. Although this apparatus is not extremely sensitive, it is handy to use, and it is believed that it gave sufficiently accurate results to show the relative value of these containers.

In operation, the container was sealed on the diffusion apparatus by immersing the open end in a mercury bath to insure an air tight seal. Then, the intake tube of the apparatus was connected to a nitrogen tank by rubber tubing and the outlet tube also extended by rubber tubing to allow the far end to be submerged in water. The bubbling of gas in the water was an indication that the nitrogen flush gas was passing through the apparatus under a constant pressure at all times.

After the apparatus had been flushed out and the stopcocks closed, a sample of the gas was obtained in a 250 milliliter gas sampling bulb. This was analyzed to obtain the original oxygen concentration inside the apparatus. At the end of a suitable diffusion period, varying with the container, a final gas sample was obtained and analyzed for oxygen concentration. Since the samples of gas were at a low temperature when taken, and the analysis apparatus could not be operated at that temperature; a one and one-half hour period

was allowed for the gas sample to attain room temperature before the analysis was run. This time lag made necessary a minimum time of two hours that any one container could be tested. Due to the rapid rate of penetration of oxygen into three of the containers tested, it would have been desirable to run tests on them for only one hour or even less before obtaining the final sample.

For the purpose of calculations, the volume of each container and of the diffusion chamber was obtained by water displacement. It was also necessary to figure the area exposed to diffusion on each container.

A comparable unit of measure between containers was obtained through use of the following formula:

$$\frac{\text{Volume of gas in diffusion chamber and sack}}{\text{Sack or container area exposed to air}} \times \frac{\text{increase in } O_2 \text{ concentration}}{\text{time}} = \text{rate/unit/unit area time}$$

An example from the kraft bag:

$$\frac{(295 + 670) \times .117}{394.7 \times 12.5} = .0346 \text{ ml/sq cm/hr.}$$

RESULTS

It was concluded that there is a significant difference between the cartons tested, as far as their value as a barrier to oxygen penetration is concerned.

The Polythene and cellophane bags approached a glass beaker as oxygen barriers under the test conditions described. The

heat-seal obtained by using a hot iron on the film bags resulted in a more nearly gas-resistant container than was formed by placing the lids on the rigid containers. It was also concluded that with a properly sealed lid, the two rigid containers, which were designed for frozen foods, would become better packaging mediums. However, this would not markedly improve the value of the ice cream carton. The kraft bag did not appear to be an efficient oxygen barrier. It is believed that a test of the basic sheet material would not prove as efficient for the kraft bag material as for either the waxed or the laminated carton basic materials. This conclusion was reached by comparing the increase in oxygen concentration for the waxed carton, the laminated carton and the kraft bag when the factory sealed end or the lid was exposed to the air. The data would tend to show that these two cartons formed a much better oxygen barrier at their factory sealed ends than in the lids, while the kraft bag appeared to have about the same values either way. This would indicate that the majority of the gas was diffusing through the kraft bag material rather than through the sealed end. The only other conclusion that could be drawn about this kraft bag would be that heat sealing of the material was not satisfactory, and the nature of these tests was such that it was not possible to distinguish whether the oxygen was entering through the seal, or diffusing through the material.

The waxed carton appeared to be more efficient over all than did the laminated carton. The basic material in either of these two containers appeared to be more efficient than that of the ice cream carton. It would appear that both the material and the method of construction enter into the development of a container which is resistant to oxygen penetration.

It is believed that such analytical tests as have been carried out in this experiment should not be relied upon exclusively in rating a frozen food c ontainer. On the contrary, such tests should be used only to select those containers which are most likely to appear effective under actual conditions of handling and storage, thus eliminating excessive time spent testing poor containers. These studies supplement actual tests with hygroscopic materials.